June 11, 1962
DMIC Memorandum 153

BRAZING AND BONDING OF COLUMBIUM, MOLYBDENUM, TANTALUM, TUNGSTEN, AND GRAPHITE

DEFENSE METALS INFORMATION CENTER

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3. To assist the Government agencies and their contractors in developing technical data required for preparation of specifications for the above materials.

4. On assignment, to conduct surveys, or laboratory research investigations, mainly of a short-range nature, as required, to ascertain causes of troubles encountered by fabricators, or to fill minor gaps in established research programs.

Contract No. AF 33(616)-7747
Project No. 2(8-8975)

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BRAZING AND BONDING OF COLUMBIUM, MOLYBDENUM, TANTALUM, TUNGSTEN, AND GRAPHITE

H. E. Pattee and R. M. Evans*

SUMMARY

The design and construction of supersonic aircraft, missiles, and space vehicles have been limited by the lack of suitable high-temperature materials. The problem first became serious in the production of high-performance jet aircraft where structural materials were exposed to high-temperature engine-exhaust products and the airframe was subjected to aerodynamic heating. The refractory materials have been considered for such applications and used to some extent; however, full realization of their potentialities has not been achieved partly due to the lack of knowledge needed to fabricate them efficiently.

Many of the important developments in the joining of columbium, molybdenum, tantalum, tungsten, and graphite are summarized in this memorandum. Much of the subject matter is devoted to the brazing processes, but diffusion and solid-state bonding are covered also. Although problems are encountered in welding the refractory metals, the subject has been covered adequately in the current literature and in other publications of the Defense Metals Information Center (DMIC).

The particular properties which recommend the refractory metals and graphite to aerospace applications are discussed. Adverse properties which limit the use of these materials or which must be overcome by using special precautions also are mentioned. Typical filler metals used to join the refractory materials for low- as well as high-temperature service conditions are covered. However, to reflect the current interest in these materials accurately, the memorandum emphasizes the high-temperature aspects of joining.

The information incorporated in this memorandum was gathered from the current literature on joining and from the open DMIC files. The most recent data on high-temperature joining are contained in reports emanating from research programs sponsored and directed by various Government agencies, particularly those involved in aircraft and missile development. A limited number of contacts with industry were made to learn about current developments and problems. Considerable work is being done by private organizations, but the results of most of these programs are considered proprietary. Patents describing joining processes, filler metals, etc., for use with the refractory metals and graphite are not included.

Although considerable information on joining the refractory materials can be obtained from the references contained in this memorandum, new data constantly are being produced by current research programs in this fast-moving field. It is suggested that recognized authorities be contacted when problem areas are encountered. Also, DMIC publications which report

*Metals Joining Research Division, Battelle Memorial Institute.

current progress in the unclassified technology of the refractory metals and graphite should be followed for the latest developments. Those holding proper clearances and the need-to-know will find much useful information in the classified literature.

INTRODUCTION

The fabrication of primary structures and components for aircraft, missiles, and related space-age developments has resulted in innumerable problems in the materials field. Current and future design concepts demand materials with high strength-to-weight ratios at temperatures ranging from subzero conditions to several thousand degrees F. The materials also must possess adequate resistance to oxidation, corrosion, and erosion and must be readily fabricable into complex configurations. The design requirements have prompted extensive research to develop and to evaluate new materials where conventional ones no longer suffice. The technology has advanced to the extent that the refractory metals appear to be among the most promising of the new structural materials. The degree of interest in these metals can be judged from the programs under way to determine the physical and mechanical properties of the refractory metals under simulated service conditions and to learn more about fabrication techniques. Graphite also is being investigated because of its possible uses at very high temperatures.

It is difficult to define the term "refractory metal" exactly but, on the basis of melting temperatures and other physical characteristics, most authorities include the following metals under this classification: chromium, vanadium, rhodium, columbium, iridium, ruthenium, hafnium, molybdenum, tantalum, osmium, rhenium, and tungsten. Because of cost, availability, properties, etc., only columbium, molybdenum, tantalum, and tungsten have become important as structural materials. Insofar as the refractory metals are concerned, this memorandum is limited to a consideration of these four metals. Because graphite has assumed such importance in applications closely akin to those for which the refractory metals are best suited, material on joining graphite is included in this memorandum.

The ability of the refractory metals to function at very high temperatures has long been recognized in other industries. However, in most cases, the service conditions were not so severe as now contemplated, and the structures were easier to fabricate. For example, most of these metals have been used as structural materials in electron tubes and similar devices; tungsten also is used widely as a filament material. The properties of these metals permit their use in many other fields. Molybdenum and columbium are useful in nuclear reactors because of their low capture cross sections to thermal neutrons. Because of its excellent resistance to corrosion by various media, tantalum is used extensively in the chemical industry. A more recent use of tantalum is in the production of electrolytic capacitors. All of the refractory metals are used as alloying elements in the production of high-strength alloys. The industrial uses of graphite are almost limitless. It is used for power-tube anodes, as a mold material in casting, for furnace and arc-lamp electrodes, and in combination with various metals for powder-metallurgy applications.

This memorandum is concerned with nonfusion methods of joining the refractory metals and graphite. In such processes, joining is accomplished at temperatures considerably below the melting points of the base material. A filier metal may, or may not, be used. These processes are important from the production standpoint because many assemblies can be joined simultaneously. Large complex configurations, such as thrust chambers, can be joined in a single operation. However, if desired, components can be added to partially completed units by using successively lower melting filler metals. Some advantages of the nonfusion joining processes which are particularly useful when joining these materials are:

(1) Dissimilar metals and some nonmetals can be bonded.

(2) Joining can be accomplished at temperatures below the recrystallization temperature of the base metal.

(3) Joints with large areas can be made, and materials of different thicknesses can be joined.

(4) Assemblies can be bonded without incurring residual stresses in the finished part.

(5) Atmospheric contamination of the base metal can be avoided by proper selection of the joining facilities.

Considerable knowledge is needed to achieve consistent bonding of the refractory metals and graphite. This includes a thorough knowledge of their characteristics and properties and the recognition that precautions may be necessary to overcome some of their adverse properties. Surface preparation of the refractory metals is important because oxides form and inhibit wetting and flow of the filler metals. In the case of solid-state bonding, surface contaminants may prevent the diffusion needed for joining. The properties of the refractory metals may be affected adversely by certain atmospheres normally associated with brazing, so knowledge about the variables inherent in the joining processes is needed also.

MATERIAL REQUIREMENTS

To understand why graphite and the refractory metals are being considered for aircraft, missile, and space-vehicle applications, it is necessary to examine the environments in which these craft operate and the problems which are encountered. This information has an important bearing on the selection of the joining process. For example, sections of the airframe of experimental rocket aircraft are subjected to aerodynamic heating in flight; during a recent test, the leading edges of such a craft reached temperatures in excess of 1000 F (538 C). In missile applications, the nose cones reach temperatures of several thousand degrees under re-entry conditions. Even more severe conditions are encountered by the materials used in rocket motors. The rocket-exhaust environment is characterized by temperatures of 6000 F (3316 C) and higher, supersonic gas flow, reactive and abrasive combustion products, and steep temperature gradients.

The ideal structural material for such applications would have the following characteristics: low specific gravity; high-melting temperature; good thermal conductivity; good thermal-shock resistance; resistance to oxidation, corrosion, and erosion; and adequate strength and ductility at both high and low temperatures. Also, it should be readily available and easy to fabricate. Although neither graphite nor the refractory metals meet all of these qualifications, they most nearly satisfy them.

REFRACTORY METALS

Properties

It is not the intention of this memorandum to provide extensive information on the properties of the refractory metals, because other DMIC reports and memoranda have covered this subject in detail. A few properties of the refractory metals are presented in Table 1 so they can be compared with those of the more conventional structural metals.[1,2]*

At temperatures above 2000 F (1093 C), the alloys of nickel and iron are generally unsatisfactory for structural purposes. They all melt below 2600 F (1427 C) and have little strength at temperatures near the melting point. Their vapor pressure is also high under these conditions, and they have little resistance to oxidation. Although the density of the refractory metals is generally high when compared with other metals, they have relatively high strength-to-weight ratios at very high temperatures. Tungsten and molybdenum have good thermal conductivities.

Problem Areas

The refractory metals have certain adverse properties which limit their usefulness and which also can affect their joining characteristics. These properties are discussed briefly so precautions can be taken when necessary.

Oxidation Characteristics

Among the most serious deficiencies of the refractory metals is their general lack of oxidation resistance, even at relatively low temperatures. For example, tungsten begins to oxidize at about 750 F (399 C) and oxidation is rapid at about 1100 F (593 C); above 1400 F (760 C) the trioxide volatilizes. Tantalum also begins to oxidize at 750 F and catastrophic oxidation occurs above 2550 F (1399 C). Molybdenum is the least oxidation resistant of the refractory metals, since a volatile oxide forms above 1200 F (649 C). Columbium oxidizes at a slower rate than do the other three metals.

*References are listed on pages 18 to 21 of this memorandum.

TABLE 1. SELECTED PROPERTIES OF SOME STRUCTURAL MATERIALS[1,2]

Metal	Density, g/cc at 20 C	Melting Point, C	Thermal Conductivity, $cal/cm^2/C/cm$	Coefficient of Linear Thermal Expansion, $cm/cm/C \times 10^{-7}$	Vapor Pressure, Torr (1.316×10^{-3} atm)	Young's Modulus (20 C), psi
Nickel	8.90	1453	0.198 at 100 C 0.175 at 200 C 0.152 at 300 C 0.142 at 400 C 0.148 at 500 C	133 from 25 - 100 C 144 from 25 - 300 C 155 from 25 - 600 C 163 from 25 - 900 C	10^{-8} at 912 C 10^{-4} at 1247 C 10^{-2} at 1497 C 10^{-1} at 1667 C	30×10^{-6}
Iron	7.87	1537	0.163 at 100 C 0.147 at 200 C 0.081 at 800 C	121 from 20 - 100 C 134 from 20 - 300 C 147 from 20 - 600 C 150 from 20 - 900 C	10^{-8} at 877 C 10^{-4} at 1207 C 10^{-2} at 1467 C 10^{-1} at 1637 C	28.5×10^{-6}
Columbium	8.57	2468 ± 10	0.125 at 0 C 0.135 at 200 C 0.145 at 400 C 0.156 at 600 C	73.9 from 0 - 400 C 75.6 from 0 - 600 C 77.2 from 0 - 800 C 78.8 from 0 - 1000 C	2.00×10^{-4} at 2031 C 1.85×10^{-4} at 2323 C	12.4×10^{-6}
Molybdenum	10.22	2620 ± 10	0.298 at 204 C 0.289 at 427 C 0.272 at 649 C 0.254 at 871 C 0.215 at 1649 C 0.206 at 2204 C	54.3 from 20 - 149 C 51.9 from 20 - 482 C 53.6 from 20 - 649 C 58.0 from 20 - 982 C 62.8 from 20 - 1316 C 66.5 from 20 - 1593 C	10^{-8} at 1582 C 10^{-4} at 2167 C 10^{-2} at 2627 C 10^{-1} at 2927 C 1 at 3297 C	47×10^{-6}
Tantalum	16.6	2996	0.130 at 20 C 0.162 at 568 C 0.171 at 828 C 0.179 at 1106 C 0.188 at 1416 C	65 from 0 - 1000 C 66 from 20 - 500 C 73 from 27 - 1400 C 78 from 27 - 2400 C	10^{-8} at 1957 C 10^{-4} at 2587 C 10^{-2} at 3067 C 10^{-1} at 3372 C 1 at 3737 C	27×10^{-6}
Tungsten	19.3	3395 ± 15	0.31 at 20 C 0.275 at 927 C 0.268 at 1127 C 0.260 at 1327 C 0.253 at 1527 C 0.245 at 1727 C	44.4 at 27 C 51.9 at 1027 C 72.6 at 2027 C	10^{-8} at 2077 C 10^{-4} at 2957 C 10^{-2} at 3297 C 10^{-1} at 3642 C	50×10^{-6}
Graphite	1.7	3652 - 3697[a]	0.02 - 0.5 at 20 C	10 - 50 at 20 C (varies widely)	10^{-8} at 1950 C 10^{-4} at 2380 C 10^{-2} at 2700 C 10^{-1} at 2900 C 1 at 3140 C 10^{-2} at 3800 C	$0.8 - 1.4 \times 10^{-6}$ (varies widely)

(a) Sublimation temperature.

The lack of oxidation resistance has hindered the development of the refractory metals, and extensive programs have been launched to find protective coatings for these metals. Progress in this area has been reported in earlier DMIC reports and memoranda. The current literature also contains references to coatings.

The characteristics of the coating and the coating process are important from the joining standpoint, because the two operations must be compatible. To afford maximum protection, assemblies should be joined first and then coated.

Reactions With Gases

The refractory metals are normally joined in an inert atmosphere or in a vacuum to avoid contamination by oxygen, nitrogen, or hydrogen. Absorption of these gases generally begins at relatively low temperatures and accelerates as the temperature increases. Tantalum begins to absorb nitrogen and hydrogen at about 1100 to 1200 F (593 to 649 C); in both cases embrittlement of the base metal occurs. Nitrogen dissolves rapidly in molybdenum above 2200 F (1204 C) and forms a brittle compound. The properties of tungsten and columbium also are impaired by similar gaseous reactions.

Recrystallization

A knowledge of the recrystallization temperature of the refractory metals and their alloys is important because a loss in base-metal properties occurs when this temperature is exceeded. Even though a completed assembly may be used at temperatures above recrystallization, it is a good policy to perform the joining operations at temperatures below that at which recrystallization occurs. The exact temperature of recrystallization is difficult to specify since it depends on many factors: time at temperature, alloy composition, impurities, etc. Recrystallization temperatures of the refractory metals range from about 1800 (982 C) for unalloyed molybdenum to about 2800 F (1538 C) for unalloyed tungsten. Alloy development programs have been established to produce refractory-metal alloys with higher recrystallization temperatures. The success of these efforts can be judged by experimental data which indicate that complete recrystallization of a molybdenum alloy (Mo-1.25Ti-0.15Zr-0.15C) requires a temperature of 2800 F.[3,4]

Ductile-to-Brittle Transition

The ductile-to-brittle transition characteristics of molybdenum and tungsten have seriously hindered their development, because both are brittle at room temperature; the transition temperature for recrystallized molybdenum and tungsten is -30 to 25 C and 150 to 315 C, respectively. Columbium does not suffer from this drawback since its transition temperature is much lower, -100 to -195 C. The transition temperature of tantalum is less than -195 C, if it exists at all.

It is not possible to furnish extensive information on ductile-to-brittle transition in this memorandum. However, an earlier DMIC report states that the transition temperature is affected by recrystallization, grain size, interstitial content, cold work, and strain rate. There apparently is a relation between transition behavior and the periodic arrangement of the elements.[5]

The importance of the joining process can be seen by its effect on the transition temperature. For example, diffusion of a brazing alloy into the base metal during brazing may cause recrystallization of the base metal; recrystallization generally increases the transition temperature. This temperature is raised also by increased grain size and by higher interstitial contents, both of which can occur during the joining operation.

GRAPHITE

Properties

Graphite has been considered as a high-temperature structural material because it has a sublimation temperature of 6605 to 6686 F (3652 to 3697 C). Graphite has an acceptable strength-to-weight ratio at very high temperatures. The potential of this material has been enhanced by the development of graphite with controlled crystal orientation. This type of graphite is strongly anisotropic in its thermal and electrical properties. Of particular interest in heat-sink applications is the fact that the thermal conductivity is several orders of magnitude greater in the plane parallel to the surface than in that at right angles to the surface. Oriented graphite has a high density and is quite impervious to gases. Some properties of graphite are shown in Table 1.

Problem Areas

The greatest difficulty in joining graphite to itself or to other materials is that graphite is not wet easily by brazing filler metals. In this respect it resembles many of the ceramic materials. Graphite can be plated with a metal which can be readily brazed; however, this expedient is suitable only for low-temperature applications.

Graphite is subject to oxidation as well as to erosion by fast-moving gases. Graphite begins to oxidize at about 840 F (450 C). The oxidation rate increases rapidly to about 2190 F (1200 C), and then becomes almost constant. Numerous research programs have been initiated to develop protective coatings for graphite, and considerable progress has been reported in the literature.

BRAZING MATERIALS

For service temperatures less than 1000 F (538 C), all of the refractory metals have been brazed with conventional silver-, gold-, and copper-base alloys.(6) Furnace-brazing procedures are usually used, and brazing is accomplished in an inert atmosphere or in a vacuum. Brazing for high-temperature service conditions is a more specialized undertaking, and several programs have been conducted to evaluate existing alloys and to develop new ones for specific applications. These developments are reviewed in the sections which follow. Until recently, efforts were concentrated on molybdenum, because it was the most advanced of the refractory metals in terms of alloy development and availability. Tungsten and graphite are now receiving the major share of attention.

Brazing Alloys for Molybdenum

An extensive program to evaluate filler metals for brazing molybdenum was conducted several years ago.(7) Molybdenum joints were brazed with the alloys listed in Table 2, and tensile tests were performed at room temperature and at 1800 F (982 C). Difficulty was experienced in determining the mechanical properties of the brazed joints because of recrystallization and the notch sensitivity of the base metal. The best short-time tensile properties were obtained with Haynes Alloy No. 25 (55Co-20Cr-15W-10Ni) and with Inconel (80Ni-14Cr-6Fe). Molybdenum also can be brazed with many of the silver- and gold-base filler metals.

Difficulties can be experienced with brazed joints because of diffusion at high service temperatures. In a recent investigation it was noted that a brittle nickel-molybdenum-gold intermetallic formed when molybdenum joints brazed with the nickel-gold eutectic alloy were exposed at high temperatures for lengthy periods.(8) The room temperature strength of such joints was low because of the brittle compound.

In the same study, molybdenum joints were diffusion bonded with nickel as the intermediate material. Nickel and molybdenum form a eutectic at about 2400 F (1320 C). The remelt temperature of these joints was nearly as high as the melting point of molybdenum.

Another study indicated that all of the major heating processes could be used to braze molybdenum. The most satisfactory joints were made with a palladium-base alloy; some nickel-base alloys were used with a chromium diffusion barrier.(9)

Brazing Alloys for Columbium

Research in the development of filler metals for brazing columbium has been directed toward high-temperature applications. A current program is being conducted to find suitable alloys for joining Cb-1.0Zr and F-48

TABLE 2. FILLER METALS FOR BRAZING MOLYBDENUM

Alloy Composition, per cent	Liquidus, F
100 Cu	1980
100 Ni	2650
100 Pd	2860
100 Pt	3225
78Ni-18Cr-4B	1950
84Ni-16Ti	2350
57Ni-17Mo-16Cu-6Fe-4W	2380
70Ni-30Cu	2460
80Ni-14Cr-6Fe	2540
18Cr-8Ni-74Fe	2600
25Cr-20Ni-55Fe	2650
54Co-27Cr-6Mo-3Ni	2550
55Co-20Cr-15W-10Ni	2600
52Nb-48Ni	2175
93Pd-7Al	2150
53Pd-47Ni	2200
60Pd-40Ni	2300
60Pd-40Cu	2200
65Pd-35Cu	2300
70Pd-30Cu	2400
50Pd-50Ag	2400
60Pd-40Ag	2500
70Pd-30Fe	2400
50Pd-50Fe	2400
Mo-B eutectic	3450
Mo-Ru	3450

(Cb-15W-5Mo-1Zr) for service in the 2000 to 2500 F range (1090 to 1370 C). Possible alloy systems were studied and the filler metals listed in Table 3 were prepared for evaluation.(10)

In future work on this program, brazed panels will be made and exposed under simulated service conditions and the properties of the joint will be studied further.

A series of filler metals was developed to braze columbium assemblies for reactor applications.(11) The binary systems of columbium, zirconium, titanium, molybdenum, and tantalum were examined for possible compositions which would have the desired melting range, flow characteristics, mechanical properties, and resistance to liquid metals. The zirconium- and titanium-base alloy systems appeared to hold the most promise. The melting points of approximately 250 alloy compositions were determined and those alloys melting below 1300 C were evaluated further by wetting tests. On the basis of their performance in wetting tests, the alloys listed in Table 4 were selected for further study. Additional samples will be brazed and examined metallographically in the as-brazed condition and after aging. Reactions with the base metal will be investigated, and the mechanical properties of brazed joints will be obtained.

Brazing Alloys for Tungsten

Tungsten can be joined with many of the filler metals which can be used with molybdenum; in addition, other refractory metals can be used to produce joints in tungsten.(12) In another phase of a program already mentioned(10), the following alloys were selected to braze unalloyed tungsten: 80Cb-20V, 85Cb-15Ni, 75Ta-25Ti, 75Ta-25V, 80Cb-20Ti, 75Ta-25Pd, and 70Mo-30Ti. No data on the properties of joints brazed with these alloys are available at the present time.

The objective of another current research program is to develop low-temperature brazing alloys to join tungsten for high-temperature service.(13) The joints are brazed at temperatures below that at which tungsten recrystallizes; a subsequent heat treatment promotes diffusion in the interfacial area to increase the remelt temperature. The platinum-boron and iridium-boron alloy systems have been studied extensively. Various proportions of tungsten powder have been added to selected alloy compositions to effect an increase in the remelt temperature. Some results of this program are shown in Table 5.

Other joints have been brazed with the iridium-boron alloy plus additions of osmium, ruthenium, or rhenium powders. None of these additions increased the remelt temperature significantly.

Brazing Alloys for Tantalum

Little research has been undertaken on the development of high-temperature brazing alloys for tantalum. However, it is expected that

TABLE 3. FILLER METALS FOR BRAZING COLUMBIUM ALLOYS

For Use With Cb-1.0Zr	For Use With F-48
95Ti-5Fe	100 Ti
80Ti-20Fe	70Ti-30V
90Ti-10Cr	78Zr-22Cb
89Zr-11Al	80V-20Ti[a]
79Ti-13Fe-8Cr[a]	65V-35Cb[a]
56Zr-28V-16Ti[a]	99Cb-1B
	97.8Cb-2.2B
	50.5Ta-49.5Zr
	66Zr-34Ta
	97Cb-3B

(a) These alloys have been examined for compatibility with the respective base metals. The maximum depth of reaction for each filler metal-base metal combination was determined for a specified brazing cycle. The braze contact angles were measured to evaluate the wetting properties of the brazing alloys.

TABLE 4. EXPERIMENTAL ALLOYS FOR BRAZING COLUMBIUM

Alloy Composition, per cent	Flow Point, C
67Zr-29V-4Fe	1300
60Zr-25V-15Cb	1280
48Zr-48Ti-4Be	1050
63Ti-27Fe-10Mo	1250
63Ti-27Fe-10V	1280
68Ti-28V-4Be	1250
45Ti-40Zr-15Fe	1050
75Zr-19Cb-6Be	1050
46Ti-46Zr-4V-4Be	1000
95Zr-5Be	1000
62Ti-26Fe-8Mo-4Zr	1250
80Zr-17Fe-3Be	1000

TABLE 5. REMELT TEMPERATURES OF TUNGSTEN LAP JOINTS BRAZED AT 2000 F AND DIFFUSED AT 2000 F FOR 3 HOURS

Basic Alloy	Percentage		Remelt Temperature, F
	Basic Alloy	Tungsten Powder	
Pt - 3.0B	89	11	3870
Pt - 3.6B	89	11	3930
Pt - 4.5B	100	0	3720
Pt - 4.5B	89	11	3850
Pt - 4.5B	80	20	3790
Pt - 4.5B	70.6	29.4	3740
Pt - 4.5B	65	35	3720
Pt - 4.5B	61.6	38.4	3750
Ir - 2.7B	100	0	3730
Ir - 2.7B	89	11	3350
Ir - 2.7B	80	20	3000
Ir - 2.7B	70.6	29.4	3830
Ir - 3.0B	100	0	3842
Ir - 3.0B	89	11	3840
Ir - 3.0B	80	20	3840
Ir - 3.0B	70.6	29.4	3450
Ir - 3.5B	100	0	3800

programs devoted to columbium and tungsten will produce results which can be applied to tantalum.[14]

Brazing Alloys for Graphite

The literature does not contain many references to brazing graphite for high-temperature services; however, this is understandable because graphite is inherently difficult to braze. In a study to develop oxidation-resistant brazing alloys, it was noted that graphite could be brazed to itself and to various metals if carbide formers were present at the interface during brazing.[15] Graphite can be brazed with a nickel-gold alloy with an addition of 6 per cent chromium; if the chromium content is reduced below 4 per cent, brazing does not occur. However, graphite can be brazed to stainless steel with the nickel-gold eutectic alloy because carbide formers are dissolved out of the stainless steel by the molten filler metal. During these studies, graphite was brazed to such metals as stainless steel, carbon steel, molybdenum, and copper. In another investigation, leak-proof joints of graphite to Nilo-K were made in order to measure the permeability of graphite at temperatures up to 1650 F (900 C) under high pressure conditions.[16] The filler metal was the silver-copper eutectic alloy with an addition of 12 per cent titanium; brazing was done in a vacuum. Some difficulty was experienced because of the differences in the coefficients of expansion between the two base materials; however, the difficulty was overcome by proper joint design.

SELECTED JOINING APPLICATIONS

Several applications have been selected to illustrate joining of the refractory metals. It is impossible to cover all the details of the joining processes in this report, but the references and bibliography may be consulted for additional information.

Tungsten-to-Graphite Brazing

Tungsten, graphite, and composite structures of these materials are being considered for many rocket-motor applications. The development of solid rocket propellants has produced exhaust temperatures of 6000 F (3300 C). Structural materials must withstand these temperatures and have adequate resistance to corrosion and erosion. Composite structures have been developed for this purpose because of the high density of tungsten. To produce lightweight structures, tungsten is used as a thin protective sheet and graphite serves to maintain structural integrity and as a heat sink. The tungsten must be well bonded to the graphite to accomplish these objectives.

Brazing With Metallic Filler Metals

Several studies have been undertaken to braze at relatively low temperatures and depend on alloying to obtain high remelt temperatures. For example, this occurs when tungsten or molybdenum is added to a commercial high-temperature brazing alloy. Among the problems encountered are recrystallization of the base metal and the formation of low-melting eutectics in the joint area. Practically all such work is being conducted under classified development programs.

Bonding With Metal Compounds

A comprehensive program to bond tungsten to graphite with metal compounds was conducted.[17] It was necessary to develop techniques to combine the graphite-to-carbide system and the carbide-to-tungsten system. It was found that a liquid phase had to be formed to obtain satisfactory carbide-to-graphite bonding; the graphite surface is impregnated to a small depth with the desired metal carbide. The most consistent bonds were obtained by (1) coating the graphite surface with a powder slurry consisting of 60Ta-10ZrH$_2$-30W, (2) drying the slurry-coated graphite and firing at 5400 F, (3) coating the tungsten surface with a ZrC powder slurry and placing it in contact with the coated graphite surface, and (4) firing the assembly at 4400 F. Successful joining was not achieved above 4700 F because a reaction between the furnace atmosphere and the tungsten resulted in formation of a low-melting liquid phase. Other metal compounds such as WC, TiC, MoC, TaC, HfC, ZrC, $TaSi_2$, TiB_2, and ZrB_2 were evaluated; however, the Ta-ZrH$_2$-W mixture produced the most satisfactory bonds.

Tungsten-to-Tungsten Brazing

Nozzle liners have been fabricated by brazing washers of tungsten together and machining the brazed assembly to the required contour.[18] A series of brazing alloys was evaluated in the preliminary stages of the program, and the following were selected for diffusion studies: Premabraze 101 (54Pd-36Ni-10Cr), titanium-nickel (50Ti-50Ni), Coast 62 (68Mn-16Ni-16Co), GE J8100 (70Ni-20Cr-10Si), and LM Nicrobraz (83.5Ni-6.5Cr-2.5Fe-3.0B-5.0Si-0.15C). Tungsten joints made with these alloys were given diffusion treatments at various temperatures for several hours in order to increase their remelt temperatures. Remelt temperatures of 4000 to 6000 F (2204 to 3316 C) were obtained with GE J8100, LM Nicrobraz, and Coast 62. Tungsten nozzle liners were fabricated with these alloys and evaluated by firing tests; the liner brazed with Coast 62 was the most successful.

Lap joints of commercially pure and 1 per cent thoriated-tungsten strip have been made using nickel or palladium as the filler metals.[19] The nickel or palladium was electroplated on the tungsten surfaces. The joints were made at temperatures between 1650 and 2010 F (900 and 1100 C) in a hydrogen atmosphere under pressures of 10,000 psi. Successful joints were accompanied by recrystallization at the joint interface. It was difficult to achieve bonding at temperatures below 2010 F (1100 C) because of improper contacting of the mating surfaces and because of incomplete recrystallization. Joints brazed at 2010 F (1100 C) for more than 10 minutes did not fail in the joint area.

Cladding With Columbium and Molybdenum

A program was initiated to fabricate composite sheets consisting of Type 301 stainless steel clad with columbium or molybdenum.(20) The following materials were used as barrier layers to limit diffusion: copper, nickel, titanium, iron, tantalum, Monel, palladium, platinum, chromium, 85-15 silver-manganese, and 70-30 palladium-silver. The composite sheets were made by hot pressing the assemblies at temperatures ranging from 1470 to 2190 F (800 to 1200 C) under pressures of 2000 psi. The extent of diffusion was determined after a 1 to 5-day treatment at 1830 F (1000 C). The most suitable barrier material for the molybdenum-stainless steel composite was nickel; iron was most satisfactory for the columbium-stainless steel composite.

Tantalum-Copper Composites

Composite materials were fabricated for nose-cone applications using the ability of copper to act as a heat sink and extract heat from an outer layer of tantalum.(21) The composite plates had to withstand a considerable degree of cold forming. An extensive program was undertaken to select suitable brazing alloys from among the available copper-, silver-, gold-, iron-, and manganese-base alloys. On the basis of their brazing characteristics and commercial availability, the following alloys were most suitable in joining tantalum to copper: 92Cu-8Sn, 82Au-18Ni, and 85Ag-15Mn.

Gas-Pressure Bonding

The bonding of the refractory metals has been accomplished by a solid-state bonding technique using gas pressures at elevated temperatures.(22) The same technique has been used to clad refractory-metal matrix dispersions. This is a particularly useful process for the refractory metals since atmospheric contaminates, such as oxygen and nitrogen, can be eliminated during the bonding cycle.

In this process, the components to be bonded are cleaned and assembled into a pressure-tight envelope. The parts are then heated to the desired temperature in an autoclave containing an inert gas at high pressure. The mating surfaces are held in intimate contact for a period sufficiently long to permit solid-state diffusion to occur between the parts.

The self-bonding of columbium can be achieved at temperatures of 2100 to 2300 F (1150 to 1260 C) with 10,000-psi pressure. Temperatures of 2300 to 2600 F (1260 to 1425 C) for molybdenum, 2600 F (1425 C) for tantalum, and 2800 F (1540 C) for tungsten at a pressure of 10,000 psi for times of 2 to 4 hours have produced satisfactory self-bonding of these materials. Bonding is normally performed at temperatures above the recrystallization temperature of the base metal to produce grain growth across the interface.

Molybdenum-to-Graphite Brazing

A study was made to determine the bonding characteristics of graphite for reactor applications.[23] Since it is known that graphite can be wet readily by metals which have a strong tendency to form carbides, efforts were concentrated on a study of alloy systems containing titanium, zirconium, tantalum, columbium, and molybdenum. The particular systems investigated were Ni-Mo, Ni-Cb, Ni-Cb-Mo, Ni-Cb-Ta, Pd-Ni-Ta, Pd-Ni-Mo, Au-Ni-Ta, and Au-Ni-Mo. Graphite tubes were brazed to molybdenum transition rings with the 48Ti-48Zr-4Be alloy. Another promising alloy for this application appeared to be 35Au-35Ni-30Ta.

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